# Enhanced Roughness of Graphene Foam for Optimizing Surface Active Copper With Efficient Electrochemical Detection of Nitrate

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In light of the growing concern over nitrate pollution, developing convenient and efficient electrochemical sensors for nitrate ions is crucial for enhancing the monitoring of drinking water and food safety. To improve the sensitivity and stability of copper-based electrodes for nitrate detection, the ultra-high conductivity graphene foam developed by the group is utilized as a supporting electrode for copper. By increasing the surface roughness of the graphene foam, its binding interaction with copper is enhanced, which significantly improved electron transfer efficiency and stability in the composite electrode during electrochemical nitrate detection. Concretely, the roughened graphene foam surface promotes the formation of a dense copper layer and a higher content of Cu(OH)<sub>2</sub> as well as oxygen defects, which enhances nitrate adsorption and further improves detection sensitivity. The resulting composite electrode achieves an impressive detection limit of 1.78 µм. This study demonstrates that optimizing the surface roughness of graphene foam can significantly enhance the electrochemical performance of composite electrodes, offering valuable insights for the design and development of next-generation, highly active composite electrodes.

## 1. Introduction

Nitrate plays a vital part in the process of the nitrogen cycle.<sup>[1]</sup> However, the decomposition of organic waste in soil and the

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excessive use of nitrogen-based fertilizers have resulted in widespread nitrate accumulation. This excess nitrate poses significant risks to human health, making nitrate pollution a global concern.<sup>[2,3]</sup> Consequently, timely and accurate monitoring of nitrates is essential for guiding agricultural practices and ensuring food safety.<sup>[2,4,5]</sup> Electrochemical detection offers high sensitivity, rapid analysis, simplicity, and cost-effectiveness, making it well-suited for on-site, real-time monitoring.<sup>[6–8]</sup>

Among the various materials used for the electrochemical detection of nitrate, copper has proven to be one of the most effective.<sup>[9–13]</sup> To enhance detection convenience, self-supporting electrodes are commonly fabricated.<sup>[14–18]</sup> However, pure copper electrodes are prone to corrosion and exhibit poor stability, necessitating the development of highly active and stable copper-based electrodes.<sup>[19]</sup>

Graphene materials, renowned for their exceptional conductivity, chemical stability, and mechanical strength, are considered ideal electrodes in electrochemical applications.<sup>[20–25]</sup> Therefore, a key challenge lies in integrating copper-based materials with excellent nitrate detection activity and graphene's outstanding electrochemical properties to create a new generation of highly sensitive and stable self-supporting electrodes.

In our group's previous research, we successfully developed a scalable graphene foam electrode that exhibited remarkable efficiency and stability in the electrochemical detection of small molecules, demonstrating its potential for various analytical applications. Furthermore, this graphene foam electrode has shown versatility, as it can be integrated with other materials, such as platinum (Pt)<sup>[26]</sup> and nickel (Ni),<sup>[27]</sup> to enable electrocatalytic or electrochemical detection in more complex and demanding environments. However, the inherent smoothness of the graphene foam surface broughts a significant challenge, as it limits the effective loading and distribution of metal materials, thereby reducing the potential for synergistic interactions.<sup>[28-30]</sup> Additionally, the relatively weak binding force between graphene and metal materials further constrains the regulatory effects of graphene on these metals,<sup>[31-35]</sup> which are essential for enhancing catalytic or electrochemical performance. Consequently, there is an SCIENCE NEWS \_\_\_\_\_



**Figure 1.** a) Schematic diagram of the preparation of the Cu/GF-60. Top view SEM images of b) GF, c) GF-60, d) Gu/GF, and e) Gu/GF-60. Top surface height profile images of f) Cu/GF and g) Cu/GF-60 taken by optical profilometry. h) Schematic diagram of adhesion testing between coating and substrate. i) Bar diagram of the adhesion of coatings on different substrates.

exigent demand to optimize the surface properties of graphene foam electrodes, such as by introducing roughness,<sup>[36]</sup> functional groups,<sup>[37]</sup> or porosity,<sup>[38]</sup> to facilitate better metal loading and adhesion.

In this work, we enhanced the surface roughness of a graphene foam electrode by rubbing it with sandpaper and subsequently modified its surface with a layer of nano-copper using an electrochemical deposition method for nitrate detection. The experimental results indicate that the increased surface roughness remarkably enhanced the binding strength between the graphene foam and the deposited copper. Additionally, it promotes the formation of a higher proportion of  $Cu(OH)_2$  and increases the content of oxygen defects on the surface. Consequently, the prepared copper/graphene foam electrode with enhanced roughness exhibited outstanding performance in nitrate electrochemical detection.

## 2. Results and Discussion

#### 2.1. Characterization of Electrodes

The schematic illustration of the Cu/GF-60 (GF-60, graphene foam treated with 60-grit sandpaper) preparation process is presented in **Figure 1a**. Generally, GF (graphene foam) was synthesized via blade coating followed by heat treatment under diverse temperature. First, utilizing graphene oxide (GO) as the precursor material. Precisely, graphene oxides were uniformly dispersed in ultrapure water at a ratio of 1:66. With the increase in temperature, the oxygen-containing functional moieties on graphene oxide decomposed and converted into gaseous products. The GO dispersion was thoroughly mixed using a homogenizer to achieve a uniform consistency. This well-mixed GO dispersion was then carefully applied onto a polyethylene terephthalate film, creating a GO film. The film was subsequently heated at 1300 °C for 2 h and then underwent high-temperature treatment in an argon atmosphere at 2850 °C for 1 h. After cooling to room temperature, graphene foam (GF) was successfully obtained. During this progress, the defect structure of graphene was gradually mended, promoting electron transfer and endowing the GF with high electrical conductivity  $(3.48 \times 10^4 \text{ S m}^{-1})$ . This enhanced conductivity allowed for more efficient charge movement within the material, which was crucial for its subsequent applications. It is worthy of note that the removal of oxygencontaining functional groups and the mending of defects constituted crucial steps in enhancing the properties of GF. Then, the surface of the GF was physically abrasively treated by using 60-grit sandpaper to produce GF-60. Finally, copper particles are deposited on the GF-60 surface via one-step electrodeposition.

The morphology of all samples was analyzed by scanning electron microscopy (SEM). As illustrated in Figures 1b,c, the

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Figure 2. a) Raman spectra. b) Bar diagram of the O/C ratio of GF and GF-60. c) C 1s spectra of Cu/GF-60 and Cu/GF. d) Cu 2p spectra of Cu/GF-60 and Cu/GF. e) O 1s spectra of Cu/GF-60 and Cu/GF. f) EPR spectra of Cu/GF-60 and Cu/GF.

surface of the GF is relatively flat, and it is subsequently processed with 60-grit sandpaper to create a grooved structure on its surface, thereby obtaining GF-60. Surface roughness of GF  $(Ra = 2.524 \,\mu\text{m})$  and GF-60  $(Ra = 7.299 \,\mu\text{m})$  were then measured (Figure S1, Supporting Information), demonstrating that the friction treatment with 60-grit sandpaper significantly improves the surface roughness of GF. Moreover, BET surface area measurements were performed on both GF and GF-60, revealing that GF-60 exhibits a larger specific surface area than pristine GF (Table S1, Supporting Information). As a result, the smooth surface of GF results in relatively smooth copper deposition on its surface (Figure 1d), while the rough surface of GF-60 not only greatly increases the specific surface area of electrodeposition, but also makes the deposited copper has a rough surface (Figure 1e). This was evidenced by the surface roughness measurement with Cu/GF to have a  $Ra = 4.212 \mu m$  and Cu/GF-60 to have a Ra =5.655 µm (Figure 1f,g). In addition, the Cu particles deposited on the surface of GF are dispersed (Figure S2, Supporting Information), whereas they are closely arranged on the surface of GF-60 (Figure S3, Supporting Information), indicating that the Cu distribution on the surface of GF-60 is denser. As demonstrated in the Energy Dispersive X-ray Spectroscopy (EDS) image, the copper particles situated on the surface of Cu/GF-60 displays a polyhedral form, and oxides are also detected therein (Figure S4, Supporting Information).

Further, TEM characterization was conducted on the Cu/GF-60 composite, revealing the lattice morphology of Cu catalysts and their interfacial interaction with the graphene foam substrate (Figure S5, Supporting Information). Then, to demonstrate the specific effect of increasing the surface roughness of graphene foam on the deposited copper particles, bond strength tests were conducted via the nano-scratches method (Figure 1h). The binding force between Cu and GF is 2.13 mN, while that between Cu and GF-60 is 4.1 mN (Figure 1i), suggesting that compared with the Cu layer on GF, the Cu layer on GF-60 presents greater resistance to removal. This finding implies a robust bonding interaction between the Cu layer and the GF-60 substrate. Evidently, such a strong adhesion remarkably promotes efficient electron transfer throughout the entire electrochemical reaction procedure.

Afterward, Raman spectra of Cu/GF and Cu/GF-60 were measured between 100 and 1000. The vibration peaks at 149/208/522/608 cm<sup>-1</sup> are attributed to Cu<sub>2</sub>O,<sup>[39,40]</sup> the vibration peaks at 288/469 cm<sup>-1</sup> belong to  $Cu(OH)_2^{[41-43]}$  and the vibration peaks at 122/820 cm<sup>-1</sup> belong to CuCl<sup>[44,45]</sup> (Figure 2a). The Raman peak at  $\approx$  342 cm<sup>-1</sup> corresponds to and Bg vibration modes of the Cu-O bond in CuO. The presence of this peak can be attributed to the partial oxidation of the catalyst surface in air, leading to the formation of CuO.<sup>[40,41]</sup> To further elucidate the surface components of Cu/GF and Cu/GF-60, an X-ray diffraction (XRD) test was performed. In Figure S6 (Supporting Information), GF and GF-60 comprise two sharp characteristic peaks of C (002) located at 26.6° and C (004) located at 54.7°. These observations imply that the carbon atomic structure of GF is strongly sp2-hybridized<sup>[46,47]</sup> and that the carbon lattice is not destroyed by an increase in surface roughness. For Cu/GF-60, the diffraction peaks observable at 43.3° and 50.5° can be respectively ascribed to the (111) and (200) crystal planes of Cu.<sup>[48]</sup> The diffraction peaks at 28.95°, 47.84°, and 56.78° accord with the (110), (210), and (310) crystal planes of CuCl, respectively. The diffraction peaks at  $\approx$ 36.57° and 42.40° index to the (111) and (200) crystal plane of Cu<sub>2</sub>O.<sup>[49]</sup> Notably, the diffraction peak at 23.35°,31.73°, and 34.1° can be assigned to (021), (110), and (002) crystal planes of Cu(OH)<sub>2</sub>.<sup>[50]</sup> However, with Cu/GF, only the (110) crystal plane diffraction peak of Cu(OH)<sub>2</sub> is observed at 31.39°. This might be attributed to the relatively low amount of Cu(OH)<sub>2</sub> on the GF surface. Furthermore, no CuO was found in Cu/GF-60 or Cu/GF, which can be due to the amount of CuO produced by oxidizing Cu<sub>2</sub>O being too low and below the XRD detection limit.

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Subsequently, X-ray photoelectron spectroscopy (XPS) was utilized to investigate the elemental valence states of GF, GF-60, Cu/GF, and Cu/GF-60 (Figure S7, Supporting Information). It was found that the O/C ratio of GF is 0.5025%, while that of GF-60 is 0.8176% (Figure 2b). The higher O/C ratio of GF-60 implies the deep layers of GF contain more oxygen-containing functional groups. The different oxygen contents on the surfaces of GF and GF-60 may be one of the reasons for the different content of Cu(OH)<sub>2</sub> in Gu/GF and Gu/GF-60. Figure 2c shows the high-resolution spectra of C 1s of Cu/GF and Cu/GF-60. The peaks obtained through fitting, centered at 284.8, 285.3, and 288.5 eV, are representative of the C-C/C=C, C-O, and C=O bonds in sequence.<sup>[51,52]</sup> Obviously, C-O occupies more proportion in Cu/GF-60. For Cu 2p, the peaks at 932.4 and 952.2 eV are attributed to Cu/Cu<sup>+</sup> species<sup>[53]</sup> (Figure 2d). Another two deconvoluted peaks at 934.8 and 955.1 eV are assigned to Cu<sup>2+</sup>. This verifies that Cu elements in the Cu/GF and Cu/GF-60 catalysts exist in multiple valence states. In comparison, the peak intensity corresponding to Cu<sup>2+</sup> in Cu/GF-60 surpasses that in Cu/GF, indicating a relatively higher concentration of Cu<sup>2+</sup> within Cu/GF-60, which is strongly associated with the Cu(OH)<sub>2</sub> content. In O 1s spectra, three peaks fitted in Cu/GF and Cu/GF-60, denoting oxygen vacancy (O1), lattice O (O2), and adsorbed OH<sup>-</sup> (O3) in sequence (Figure 2e).<sup>[49,48]</sup> The percentage of oxygen vacancy (O1) in Cu/GF-60 is substantially higher than in Cu/GF, showing that oxygen defects exist in the surface oxide or hydroxide of Cu/GF-60. Hence, for further exploration, electron paramagnetic resonance (EPR) tests were carried out to investigate the oxygen vacancies (Figure 2f). By contrast, a stronger electron paramagnetic resonance (EPR) signal is exhibited by Cu/GF-60 (Figure 2f). The results are consistent with the test results of oxygen vacancy O1 in XPS, indicating the presence of unsaturated Cu atoms and oxygen vacancies, additionally verifying the existence of low coordinated Cu atoms,<sup>[54]</sup> which is beneficial for the catalytic effect on nitrate ions.

#### 2.2. Electrochemical Sensing for Nitrate Detection

To access the practicality of Cu/GF-60 in the field of electrochemical sensing, nitrate detection was carried out to explore its performance in electrochemical fields. First, inductively coupled plasma mass spectrometry (ICP) tests were conducted on Cu/GF and Cu/GF-60 to measure their Cu content. The results show that the Cu contents in Cu/GF and Cu/GF-60 are almost identical (Table S2, Supporting Information), suggesting that surface roughness solely impacts the distribution of Cu particles, not the amount deposited. In this way, it is possible to prevent the difference in electrochemical performance brought on by different amounts of Cu particle deposition.

**Figure 3**a depicts the cyclic voltammogram (CV) of Cu/GF-60 at a scan rate of 50 mV s<sup>-1</sup>. One was obtained in a mixed solution composed of 0.1 M nitrate and 0.1 M Na<sub>2</sub>SO<sub>4</sub>, while the other was recorded in a blank solution (0.1 M Na<sub>2</sub>SO<sub>4</sub> as electrolyte). Cu/GF-60 exhibits a noticeable redox peak at -0.6 and -0.2 V in blank solution, and this peak can be ascribed to the redox reaction of Cu. In contrast, Cu/GF-60 exhibits new redox peaks at -0.85, -1.15, and -1.3 V in the presence of 0.1 M nitrate, which can be assigned to the redox reaction of 0.1 M NO<sub>3</sub><sup>-</sup>. The mechanism is explained in Supporting Information.

Further, a Linear Sweep Voltammetry (LSV) test was carried out to explore the current intensities generated by different electrodes in the nitrate detection process. In 3 mm nitrate solutions, pure GF and GF-60 hardly have any current response to nitrate ions, which is due to the lack of active substances. With loading active Cu layers, Cu/GF-60 and Gu/GF show significant current density response, and the current density response of Cu/GF-60 was higher than Cu/GF (Figure 3b). Then, we also conducted comparative tests using commercial graphene membranes (GMS).<sup>[55]</sup> In the presence of nitrate, the Cu/GMS-60 electrode generated from sandpaper friction treatment had a greater current density response than the Cu/GMS electrode. In addition, Cu/GF and Cu/GF-60 consistently exhibit a higher current density response. This leads us to two conclusions. First, graphene foam works better as an electrode platform (Figure S8, Supporting Information). Second, improving the surface roughness of graphene membranes or foams can enhance the specific surface area of electrodeposited Cu, promoting electrochemical reactions.

Then, we further investigated their conductivity and discovered that the conductivity of GF and GF-60 remained constant. Cu deposits boosted the conductivity of Cu/GF and Cu/GF-60 considerably. More notably, the conductivity of Cu/GF-60 exceeds that of Cu/GF (Figure S9, Supporting Information). As a result, higher conductivity indicates faster electron transport, which contributes to the enhancement of the detection performance. Moreover, electrochemical impedance spectroscopy (EIS) reveals that the Cu/GF-60 electrode presents the lowest charge transfer resistance (Figure 3c). These results additionally corroborate the excellent electrochemical performance of Cu/GF-60 and substantiate the findings obtained from LSV.

Subsequently, CV experiments were applied over a range of scanning rates spanning from 50 to 500 mV s<sup>-1</sup> in a blended solution consisting of 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 3 mm nitrate. The intention was to explore more deeply the kinetic characteristics of nitrate reactions occurring on the active surface area of the Cu/GF-60 electrode. As presented in Figure 3d, it is observed that the anode peak current density  $(I_{na})$  and the cathode peak current density  $(I_{pc})$  demonstrate a successive upward trend in tandem with the elevation of the scanning rate. Simultaneously, the anodic peak potential  $(E_{pa})$  and the cathodic peak potential  $(E_{pc})$  shift toward more positive and more negative values, respectively. This suggests a quasi-reversible redox mode for the process under investigation. Conclusively, it is confirmed that a linear relationship existed between the intensity of the current response and the square root of the scanning rate (Figure 3e). Such a linear relationship furnishes significant insights into the electron transfer

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**Figure 3.** a) CV of Cu/GF-60 in the absence or presence of nitrate of 0.1 M KNO<sub>3</sub>. b) LSV curves and c) EIS results of bare GF, GF-60, Cu/GF, and Cu/GF-60. d) CV curves of Cu/GF-60 at different scan rates. e) The plot of peak current density against the square root of the scan rate for Cu/GF-60. f) CV curves of Cu/GF-60 with varying concentrations of nitrate. g) The plot of peak current density against the concentration of 3 mM nitrate for Cu/GF-60. h) Amperometric responses of Cu/GF-60 with successive injection of nitrate (3  $\mu$ M-5 mM) at -1 V (inset: enlarged plot in the range from 0 to 647 s). i) Linear curve peak of current density versus nitrate concentrations for Cu/GF-60.

kinetics involved in the nitrate reactions. The linear regression equation is  $I_{\rm pc}$  ( $\mu A) = -0.4782 v^{1/2} - 1.9513$  ( $R^2 = 0.991$ ) (Equation (1)), and its slope is 0.4782. It is widely acknowledged that when the slope approximates 0.5, implying that the electrochemical reaction follows a diffusion-controlled process. Conversely, if the slope is near 1, the electrochemical reaction proceeds through an adsorption-controlled process. According to Equation (1), for the Cu/GF-60 electrode, the reduction of NO\_3^- is subject to a diffusion mechanism.<sup>[56]</sup>

Immediately, the CV responses of Cu/GF-60 electrodes within electrolytes of varying nitrate concentrations were examined. As illustrated in Figure 3f, upon the successive increment of nitrate concentration spanning from 200 to 2000  $\mu$ M, the peak reduction current density exhibits a remarkable augmentation and presents a linear dependence ( $R^2 = 0.991$ ) (Figure 3g). These findings

suggest that the Cu/GF-60 electrode manifests outstanding catalytic capabilities for nitrate detection across a broad concentration spectrum. Then, the detection limit and sensitivity of the Cu/GF-60 electrode with respect to nitrate detection were appraised by amperometry techniques. Figure 3h depicts a stable amperometric response curve for the Cu/GF-60 electrode. Notably, as the nitrate concentrations augment within the range of  $3 \,\mu$ M to 5 mM, the current density response exhibits a corresponding gradual increment. Even when minuscule amounts of nitrate are introduced, the electrode still generates a conspicuous response. Figure 3i showcases the calibration curve that delineates the relationship between the steady-state current density and nitrate concentration, exhibiting remarkable linearity. Derived from the relationship between nitrate concentration and reduction current density, the regression equation is precisely



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**Figure 4.** a) Amperometric responses of Cu/GF-60 with continuous addition of ions. In the beginning nitrate (0.1 mm) and other interfering substances (0.5 mm), and in the end 0.5 mm nitrate. b) Histogram of the interfering substances current response. c) Amperometric response of Cu/GF-60 to nitrate over a long running time of 10 000 s. d) Response current density of six parallel electrodes. e) The change in current density when a sample is reused and washed repeatedly for nine times. f) CV curves of Cu/GF-60 initially and after bending at 90°. g) A three-electrode system was fabricated by laser engraving graphene foam. h) Amperometric responses with successive injection of nitrate (0.15–5 mm) in river water at -1 V. (inset: enlarged plot in the range from 0 to 650 s). i) Linear curve peak of current density versus nitrate concentrations from.

formulated as j ( $\mu$ A cm<sup>2</sup>) = -0.7924x ( $\mu$ M) - 475.675 ( $\mu$ M), exhibiting a correlation coefficient of  $R^2 = 0.990$ . where x is the concentration of NO<sub>3</sub><sup>-</sup>. Based on the linear regression equation, a sensitivity of  $0.79 \,\mu$ A/ $\mu$ M was obtained from the slope of the linear regression equation. By applying the formula LOD =  $3\sigma/S$ , the limit of detection (LOD) for the Cu/GF-60 electrode is computed to be  $1.78 \,\mu$ M (S/N = 3) at a signal-to-noise ratio of 3 (S/N = 3). Where  $\sigma$  is the standard deviation of six measurements taken from the signal obtained from the blank and S is the slope of the calibration curve. This detection limit proves to be more advantageous compared to those of the majority of the currently reported enzyme-free nitrate sensing electrodes, as elaborated in Table S3 (Supporting Information). Such superiority in performance highlights the potential of the Cu/GF-60 electrode in nitrate detection.

Apart from high sensitivity, outstanding selectivity is of crucial importance for the newly developed sensors. Given that there is invariably interference from diverse substances during nitrate detection, we herein accessed the specificity of the developed sensors to ascertain the practical applicability of the Cu/GF-60 electrode. To explore the selective electrochemical response of the Cu/GF-60 sensor with respect to nitrate, interfering substances were employed in the ensuing tests. Figure 4a presents the amperometric response of nitrate and interferents at a potential of -1 V, with an interferent concentration of 0.5 mm. 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution is used as the blank electrolyte, and then the working electrode, platinum wire electrode, and calomel electrode are immersed in the solution for testing. The area under the liquid surface of the working electrode is  $1 \times 1$  cm<sup>2</sup>. After 100 s of operation, 0.1 mm NO<sub>3</sub><sup>-</sup> is added first. Then, five times the concentration

of interfering ions are added, such as Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, Mg<sup>2+</sup>, and K<sup>+</sup>. Finally, 0.2 mM of potassium nitrate solution is added at  $\approx$ 600s. As expected, the current intensity changes significantly when NO<sub>3</sub><sup>-</sup> is added twice, and the current is almost no change when other interfering ions is added. The histogram of amperometric response illustrated in Figure 4b depicts the variation in

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when other interfering ions is added. The histogram of amperometric response illustrated in Figure 4b depicts the variation in current density with respect to nitrate and interferents, distinctly indicating that the newly developed Cu/GF-60 electrode exhibits remarkable selectivity for nitrate.

Figure 4c portrays the current density response over the continuous 10 000 s test interval subsequent to the addition of nitrate. Upon introducing 3 mm nitrate, a swift elevation in current density is discerned, and the electrical signal remains comparatively stable, exhibiting no conspicuous deterioration throughout the entire testing period. Furthermore, with the aim of probing into the reproducibility characteristics of the fabricated electrodes, six electrodes were manufactured via an identical methodology for subsequent analysis. As shown in Figure 4d, it is evident that for six electrodes in the presence of 0.1 M Na<sub>2</sub>SO<sub>4</sub>, the magnitudes of the peak currents corresponding to the redox reaction of Cu are highly comparable. The value of six peak currents are 1.56, 1.54, 1.52, 1.53, 1.51, and 1.57 mA. The relative standard deviation, calculated to be 1.68%, indicates that the Cu/GF-60 electrode exhibits outstanding reproducibility. This high level of reproducibility not only validates the reliability of the electrode fabrication process but also augurs well for its practical applications, as it ensures consistent performance across multiple samples. Moreover, the washing stability test was investigated (Figure 4e). In the nine tests, the current intensity remained relatively stable, with an RSD of 3.40%, showing good reusability. Additionally, the electrochemical characteristics of the fabricated electrode exhibit scarcely any alteration even after being bent at 90°, as shown in Figure 4f. The electrode at 0° serves as the reference sample without bending, providing a comparative baseline for the electrode bent at 90°. This indicates the outstanding flexibility of the Cu/GF-60 electrode.

Herein, for better application, we fabricated the GF into a three-electrode system by means of laser engraving technology, the schematic diagram is shown in Figure 4g. The working electrode was the Cu/GF-60 electrode prepared via the electrodeposition method. The reference electrode was formed by drop-coating AgCl electronic paste, while the counter electrode was GF without any modification. The picture of the actual samples is shown in Figure S10 (Supporting Information).

Subsequently, tests on real water samples were conducted on the home-made three-electrode system. The target analytes were introduced to river water that had been collected from the riverside. The three-electrode setup demonstrates a remarkable response in nitrate electrolytes with varying concentrations (Figure 4h). Notably, it displays an outstanding linear correlation when the concentration spans from 0.12 to 5 mm, accompanied by a correlation coefficient of  $R^2 = 0.9977$  (Figure 4i). The limit of detection (LOD) is 70 µm, with a sensitivity of 0.15 µA/µm, demonstrating its good potential for application.

## 3. Conclusion

In summary, we employed sandpaper friction to enhance the surface roughness of graphene foam with ultra-high conductivity, followed by electrodeposition to create a copper-graphene foam composite electrode. The ultra-high conductivity of graphene foam facilitates efficient electron transport within the composite electrode, significantly contributing to its overall performance. Second, the increased surface roughness of the graphene foam not only expands the contact area between the surfaceactive copper and the electrolyte but also optimizes the composition of the surface-active copper. Moreover, owing to the groove configuration present on the surface of GF-60, the Cu particles thereby formed have a higher degree of compactness, which contributes to interaction with the target molecule. Collectively, the enhanced binding strength between the roughened graphene foam and the dense active copper, coupled with the Cu(OH)<sub>2</sub> formed on the copper surface, synergistically lead to a remarkable enhancement in the nitrate electrochemical detection performance of the composite electrode. This work offers valuable insights and a promising approach to constructing self-supporting electrodes with exceptional performance characteristics.

#### 4. Experimental Section Characterizations

*Materials*: Graphene oxide (GO) was purchased from Wuxi ChengYi Education Technology Co., Ltd (China). Copper chloride hydrate (CuCl<sub>2</sub>), nitrate of potash (KNO<sub>3</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and magnesium sulfate (MgSO<sub>4</sub>) purchased from Macklin Biochemical Technology Co., Ltd (China). The river water was extracted from the lake in Ruize Industrial Park of Hainan province, Sanya city (China).

Synthesis of Graphene Foam: Graphene foam (GF) was synthesized via a high-temperature thermal reduction strategy, utilizing graphene oxide (GO) as the precursor material. Precisely, graphene oxides were uniformly dispersed in ultrapure water at a ratio of 1:66. Then, a homogenizer was employed to carry out thorough stirring of the GO dispersion to ensure homogeneity. Thereafter, the well-stirred GO dispersion was meticulously coated onto a polyethylene terephthalate film, thereby forming the GO film. Subsequently, the graphene oxide film was heated at 1300 °C for a duration of 2 h, followed by being subjected to a high-temperature treatment in an argon environment at 2850 °C for 1 h. After cooling to room temperature, GF was successfully obtained.

Preparation of Cu/GF-60: Cu/GF-60 was fabricated utilizing a facile one-step electrodeposition technique. Before modification, GF was immersed in acetone for a period of 4 h. Then, in the pretreatment stage, it was placed into a tubular furnace heated to 400 °C, and maintained at 400 °C for 2 h under an air atmosphere. The 60-grit sandpaper was fixed under 170 g weight to make a sanding device, and then the surface of GF was sanded with the sanding device. The specific method was to push the sanding device from one end of GF to the other end to form GF-60. Then, Cu was electroplated onto GF-60 using an electrochemical workstation. In this three-electrode system, the counter electrode was platinum (Pt) wire, the reference electrode was calomel electrode (SCE), GF-60 was the working electrode, and the electrolytes were 0.01 M CuCl<sub>2</sub>. During this process, the deposition current density was set at 2.5 mA cm<sup>-2</sup> and the deposition lasted for 25 min. The resulting Cu/GF-60 was washed first with deionized water and then with anhydrous alcohol. The preparation procedure of Cu-GF was consistent with the previously described method. The only difference lies in that, the surface of GF does not undergo sandpaper treatment

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

# **Keywords**

dense copper layer, graphene foam, nitrate detection, surface roughness

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